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GLASSES FOR FLAT PANEL DISPLAYS

Field of the Invention

The present invention relates to alkali-free, aluminosilicate glasses exhibiting desirable physical and chemical properties for substrates in flat panel display devices.

Background of the Invention

Displays may be broadly classified into one of two types: emissive (e.g., CRTs and plasma display panels (PDPs)) or non-emissive. This latter family, to which liquid crystal displays (LCDs) belong, relies upon an external light source, with the display only serving as a light modulator. In the case of liquid crystal displays, this external light source may be either ambient light (used in reflective displays) or a dedicated light source (such as found in direct view displays).

Liquid crystal displays rely upon three inherent features of the liquid crystal (LC) material to modulate light. The first is the ability of the LC to cause the optical rotation of polarized light. Second, is the ability of the LC to establish this rotation by mechanical orientation of the liquid crystal. The third feature is the ability of the liquid crystal to undergo this mechanical orientation by the application of an external electric field.

In the construction of a simple, twisted nematic (TN) liquid crystal display, two substrates surround a layer of liquid crystal material. In a display type known as Normally White, the application of alignment layers on the inner surface of the substrates creates a 90° spiral of the liquid crystal director. This means that the polarization of linearly polarized light entering one face of the liquid crystal cell will be rotated 90° by the liquid crystal material. Polarization films, oriented 90° to each other, are placed on the outer surfaces of the substrates.

Light, upon entering the first polarization film, becomes linearly polarized. Traversing the liquid crystal cell, the polarization of this light is rotated 90° and is allowed to exit through the second polarization film.

Application of an electric field across the liquid crystal layer aligns the liquid crystal directors with the field, interrupting its ability to rotate light. Linearly polarized light passing through this cell does not have its polarization rotated and hence is blocked by the second polarization film. Thus, in the simplest sense, the liquid crystal material becomes a light valve, whose ability to allow or block light transmission is controlled by the application of an electric field.

The above description pertains to the operation of a single pixel in a liquid crystal display. High information type displays require the assembly of several million of these pixels, which are referred to as sub pixels, into a matrix format. Addressing, or applying an electric field to, all of these sub pixels while maximizing addressing speed and minimizing cross-talk presents several challenges. One of the preferred ways to address sub pixels is by controlling the electric field with a thin film transistor located at each sub pixel, which forms the basis of active matrix liquid crystal display devices (AMLCDs).

The manufacturing of these displays is extremely complex, and the properties of the substrate glass are extremely important. First and foremost, the glass substrates used in the production of AMLCD devices need have their physical dimensions tightly controlled. The downdraw sheet or fusion process, described in U.S. patent nos. 3,338,696 (Dockerty) and 3,682,609 (Dockerty), is one of the few capable of delivering such product without requiring costly post forming finishing operations, such as lapping and polishing. Unfortunately, the fusion process places rather severe restrictions on the glass properties, requiring relatively high liquidus viscosities, preferably greater than 200,000 poises.

Typically, the two substrates that comprise the display are manufactured separately. One, the color filter plate, has a series of red, blue, green, and black organic dyes deposited on it. Each of these primary colors must correspond precisely with the pixel electrode area of the companion, active, plate. To remove the influence of differences between the ambient thermal

conditions encountered during the manufacture of the two plates, it is desirable to use glass substrates whose dimensions are independent of thermal condition (i.e., glasses with lower coefficients of thermal expansion). However, this property needs to be balanced by the generation of stresses between

- 5 deposited films and the substrates that arise due to expansion mismatch. It is estimated that an optimal coefficient of thermal expansion is in the range of $28-33 \times 10^{-7}/^{\circ}\text{C}$.

The active plate, so called because it contains the active, thin film transistors, is manufactured using typical semiconductor type processes.

- 10 These include sputtering, CVD, photolithography, and etching. It is highly desirable that the glass be unchanged during these processes. Thus, the glass needs to demonstrate both thermal and chemical stability.

Thermal stability (also known as thermal compaction or shrinkage) is dependent upon both the inherent viscous nature of a particular glass
15 composition (as indicated by its strain point) and the thermal history of the glass sheet as determined by the manufacturing process. United States patent no. 5,374,595, disclosed that glass with a strain point in excess of 650°C and with the thermal history of the fusion process will have acceptable thermal stability for active plates based both on a-Si thin film transistors (TFTs) and
20 super low temperature p-Si TFTs. Higher temperature processing (such as required by low temperature p-Si TFTs) may require the addition of an annealing step to the glass substrate to ensure thermal stability.

Chemical stability implies a resistance to attack of the various etchant solutions used in the manufacture processes. Of particular interest is a
25 resistance to attack from the dry etching conditions used to etch the silicon layer. To benchmark the dry etch conditions, a substrate sample is exposed to an etchant solution known as 110BHF. This test consists of immersing a sample of glass in a solution of 1 volume of 50 wt. % HF and 10 volumes 40 wt. % NH_4F at 30°C . for 5 minutes. The sample is graded on weight loss
30 and appearance.

In addition to these requirements, AMLCD manufacturers are finding that both demand for larger display sizes and the economics of scale are driving

- them to process larger sized pieces of glass. Current industry standards are Gen III (550mm x 650mm) and Gen III.5 (600mm x 720mm), but future efforts are geared toward Gen IV (1m x 1m) sizes, and potentially larger sizes. This raises several concerns. First and foremost is simply the weight of the glass.
- 5 The 50+% increase in glass weight in going from Gen III.5 to Gen IV has significant implications for the robotic handlers used to ferry the glass into and through process stations. In addition, elastic sag, which is dependent upon glass density and Young's Modulus, becomes more of an issue with larger sheet sizes impacting the ability to load, retrieve, and space the glass in the
- 10 cassettes used to transport the glass between process stations.

Accordingly, it would be desirable to provide a glass composition for display devices having a low density to alleviate difficulties associated with larger sheet size, preferably less than 2.45 g/cm^3 and a liquidus viscosity greater than about 200,000 poises. In addition, it would be desirable for the

15 glass to have thermal expansion between about $28-35 \times 10^{-7}/^\circ\text{C}$, and preferably between about $28-33 \times 10^{-7}/^\circ\text{C}$, over the temperature range of 0-300° C. Furthermore, it would be advantageous for the glass to have a strain point greater than 650° C., and for the glass to be resistant to attack from etchant solutions.

20 Summary of the Invention

The present invention is founded in the discovery of glasses exhibiting densities less than 2.45 g/cm^3 and a liquidus viscosity (defined as the viscosity of the glass at the liquidus temperature) greater than about 200,000 poises, preferably greater than about 400,000 poises, more preferably greater than

25 about 600,000 poises, and most preferably greater than about 800,000 poises. Additionally, the glasses of the present invention exhibit linear coefficients of thermal expansion over the temperature range of 0-300° C. between about $28-35 \times 10^{-7}/^\circ\text{C}$, and preferably between about $28-33 \times 10^{-7}/^\circ\text{C}$, and strain points higher than about 650° C. The glass of the present invention has a

30 melting temperature less than about 1700° C. In addition, the glass exhibits a weight loss of less than about 0.5 mg/cm^2 after immersion in a solution of 1 part HF 50 wt.% and 10 parts 40% wt.%NH₄F for 5 minutes at 30° C.

The glass of the present invention has a composition consisting essentially of the following composition as calculated in mole percent on an oxide basis: 65-75 SiO₂, 7-13 Al₂O₃, 5-15 B₂O₃, 0-3 MgO, 5-15 CaO, 0-5 SrO, and essentially free of BaO. More preferably, the glass of the present invention

- 5 has a composition consisting essentially of the following composition as calculated in mole percent on an oxide basis: 67-73 SiO₂, 8-11.5 Al₂O₃, 8-12 B₂O₃, 0-1 MgO, 5.5-11 CaO, and 0-5 SrO.

We have discovered that for glasses having the compositions and physical properties discussed above, especially the preferred compositions and
10 preferred properties, the liquidus viscosity of the glass is strongly influenced by the ratio of the sum of alkaline earths, RO (R = Mg, Ca, Sr) to alumina on a mol% basis, or RO/Al₂O₃ = (MgO+CaO+SrO)/ Al₂O₃. This ratio is referred to as RO/Al₂O₃, and should be held in the range 0.9 to 1.2. Most preferably, this range should be 0.92 < RO/Al₂O₃ < 0.96 to obtain the highest liquidus viscosity.

15 The glasses of the present invention are essentially free of BaO, which means that the glasses preferably contain less than about 0.1 mol % BaO. The glasses of the invention are also essentially free of alkali metal oxides, which means that the glasses preferably contain a total of less than about 0.1 mol% of alkali metal oxides. Additionally, these glasses may contain fining agents
20 (such as the oxides of arsenic, antimony, cerium, tin, and/or the halides, chlorine/fluorine).

In another aspect of the invention, the glasses have a melting temperature less than about 1700° C. The glasses of the present invention also exhibit a weight loss of less than 0.5 mg/cm² after immersion in a solution
25 of 1 part 50 wt.% HF and 10 parts 40% wt.% NH₄F for 5 minutes at 30° C. The glasses are useful as a substrate for flat panel displays. Substrates made from the glass of the present invention have an average surface roughness as measured by atomic force microscopy of less than about 0.5 nm and an average internal stress as measured by optical retardation of less than about
30 150 psi.

Detailed Description of the Invention

The present invention is concerned with improved glasses for use as flat panel display substrates. In particular, the glasses meet the various property requirements of such substrates.

- 5 The preferred glasses in accordance with the present invention exhibit a density of less than about 2.45 gm/cm³, preferably less than about 2.40 gm/cm³, a CTE over the temperature range of 0-300° C. between about 28-35 X 10⁻⁷/°C, preferably between about 28-33 X 10⁻⁷/°C, and strain points higher than about 650° C, preferably greater than 660° C. A high strain point is
10 desirable to help prevent panel distortion due to compaction/shrinkage during subsequent thermal processing.

For more demanding manufacturing conditions such as the fusion process, described in U.S. patent nos. 3,338,696 (Dockerty) and 3,682,609 (Dockerty), a glass having a high liquidus viscosity is required. Therefore, in a
15 preferred embodiment of the present invention, the glasses should exhibit a density less than about 2.45 gm/cm³ and a liquidus viscosity greater than about 200,000 poises, preferably greater than about 400,000 poises, more preferably greater than about 600,000 poises, and most preferably greater than about 800,000 poises. Although substrates made from glass of the present
20 invention can be made using other manufacturing processes such as the float process, the fusion process is preferred for several reasons. First, glass substrates made from the fusion process do not require polishing. Current glass substrate polishing is capable of producing glass substrates having an average surface roughness greater than about 0.5 nm (Ra), as measured by
25 atomic force microscopy. Glass substrates produced according to the present invention and using the fusion process have an average surface roughness as measured by atomic force microscopy of less than 0.5 nm.

Chemical durability involves a resistance to attack of the various etchant solutions used in the manufacture processes. Of particular interest is a
30 resistance to attack from the dry etching conditions used to etch the silicon layer. One benchmark of the dry etch conditions is exposure to a etchant solution known as 110BHF. This test consists of immersing a sample of glass

in a solution of 1 volume of 50 wt. % HF and 10 volumes 40 wt. % NH₄F at 30°C for 5 minutes. Chemical resistance is determined by measuring weight loss in terms of mg/cm². This property is listed in Table I as "110 BHF."

- The glasses of the present invention include 65-75 mol %, preferably 5 67-73 mol %, SiO₂ as the primary glass former. Increasing silica improves the liquidus viscosity and reduces the density and CTE of the glass, but excessive silica is detrimental to the melting temperatures. The glasses also comprise 7-13 mol %, preferably 8-11.5 mol %, Al₂O₃. Increases in Al₂O₃ content increase glass durability and decrease CTE, but liquidus temperatures 10 increase. At least 8 mol % is required to have the most desired strain point; however, more than 11.5 mol % results in a less than desired liquidus temperature.

- The glasses further include 5-15 mol %, preferably 8-12 mol % boric oxide. Boric oxide lowers the liquidus temperature and density and preferably is 15 present in at least 8 mol %; however, more than 12 mol % boric oxide will negatively impact the glass strain point.

- MgO is present in the glasses of the present invention in an amount of 0-3 mol %, preferably 0-1 mol %. Increasing MgO decreases liquidus viscosity, and therefore, no more than 3 mol % MgO should be present in the glass. 20 However, smaller amounts of MgO may be beneficial for reducing density.

- CaO is useful to lower both the melting and liquidus temperatures of the glass; however, more than 11 mol % will result in a less than desired strain point and a higher than desired coefficient of thermal expansion. Therefore, the glasses of the present invention can include 5-15 mol % CaO, but preferably 25 include 5.5-11 mol % CaO.

- The RO/Al₂O₃ ratio is in the range 0.9-1.2. Within this range local minima in liquidus temperature can be found, corresponding to cotectics and/or eutectics in the base system CaO-Al₂O₃-SiO₂. The viscosity curves of the glasses in this series do not vary significantly, thus these changes in liquidus 30 temperatures are the primary drivers for increases in liquidus viscosity.

Because of their negative impact on thin film transistor (TFT) performance, alkalis such as lithia, soda or potash are excluded from the

present glass compositions. Likewise, heavier alkaline earth metals (SrO and BaO) will be either minimized or excluded because of their negative impact on the glass density. Accordingly, the glasses of the present invention may include 0-5 mol % SrO. However, the glasses of the invention are essentially free of BaO. As used herein, essentially free of BaO means that the composition contains less than 0.1 mol % of BaO in the composition.

Fining agents such as As₂O₃, Sb₂O₃, CeO₂, SnO₂, Cl, F, SO₂, etc. may also be present to aid in the removal of seeds from the glass. The glass may also contain contaminants as typically found in commercially prepared glasses.

10 In addition, the following oxides can be added at a level not exceeding 1 mol % without pushing properties outside of the ranges described above: TiO₂, ZnO, ZrO₂, Y₂O₃, La₂O₃. Table I lists examples of glasses of the present invention in terms of mol % along with their physical properties. The comparative example in Table 1 is Corning Incorporated's 1737 glass.

15 The invention is further illustrated by the following examples, which are meant to be illustrative, and not in any way limiting, to the claimed invention. TABLE I sets forth exemplary glass compositions in mol percent, as calculated on an oxide basis from the glass batches. These example glasses were prepared by melting 1,000-25,000 gram batches of each glass composition at a 20 temperature and time to result in a relatively homogeneous glass composition, e.g. at a temperature of about 1625°C for a period of about 4-16 hours in platinum crucibles. Also set forth are relevant glass properties for each glass composition, determined on the glasses in accordance with techniques conventional in the glass art. Thus, the linear coefficient of thermal expansion 25 (CTE) over the temperature range 0-300° C. is expressed in terms of $\times 10^{-7}/^{\circ}\text{C}.$, the softening point (Soft. Pt.), and the annealing point (Ann. Pt.), and strain point (Str. Pt.) are expressed in terms of °C. These were determined from fiber elongation techniques (ASTM references E228-85, C338, and C336, respectively). The density (Den.), in terms of g/cm³, was measured via the 30 Archimedes method (ASTM C693).

The 200 poise temperature (Melt. Temp., °C) (defined as the temperature at which the glass melt demonstrates a viscosity of 200 poises [20

Pa.s]) was calculated employing the Fulcher equation fit to the high temperature viscosity data (measure via rotating cylinders viscometry, ASTM C965-81). The liquidus temperature (Liq. Temp.) of the glass was measured using the standard liquidus method. This involves placing crushed glass

5 particles in a platinum boat, placing the boat in a furnace having a region of gradient temperatures, heating the boat in an appropriate temperature region for 24 hours, and determining by means of microscopic examination the highest temperature at which crystals appear in the interior of the glass. The liquidus viscosity (Liq. Visc., in poises) was determined from this temperature and the

10 coefficients of the Fulcher equation.

Table I records a number of glass compositions, expressed in terms of parts by mole on the oxide basis, illustrating the compositional parameters of the present invention. Inasmuch as the sum of the individual constituents totals or very closely approximates 100, for all practical purposes the reported values

15 may be deemed to represent mole percent. The actual batch ingredients may comprise any materials, either oxides, or other compounds, which, when melted together with the other batch components, will be converted into the desired oxide in the proper proportions. For example, SrCO_3 and CaCO_3 can provide the source of SrO and CaO , respectively.

20 Glasses having the compositions and properties shown in Examples 14 and 19 are currently regarded as representing the best mode of the invention, that is, as providing the best combination of properties for the purposes of the invention at this time.

Although the invention has been described in detail for the purpose of
25 illustration, it is understood that such detail is solely for that purpose and variations can be made therein by those skilled in the art without departing from the spirit and scope of the invention which is defined by the following claims.

TABLE 1

Composition Batched (mol%)	1	2	3	4	5	6	7	8
SiO ₂	69.75	69.78	69.75	69.8	70.7	70.57	69.1	70.85
Al ₂ O ₃	10.2	10.2	10.3	10.3	10	9.77	10.35	9.5
B ₂ O ₃	9.7	9.7	9.5	9.5	10	9.95	10.25	10.1
MgO	0.8	0.8	0.8	0.8		0.12	0.15	1.25
CaO	7	7	8.5	8.5	9	9.17	9.8	6.7
SrO	2.2	2.2	0.8	0.8				1.3
BaO								
As ₂ O ₃	0.3		0.3	0.3		0.4	0.33	
Sb ₂ O ₃	0.3		0.3		0.3			0.1
CeO ₂								0.2
Y ₂ O ₃								
SnO ₂	0.05	0.02	0.05		0.05	0.02	0.02	
Cl	0.2	0	0.2		0.2			0.2
RO/Al ₂ O ₃	0.98	0.98	0.98	0.98	0.90	0.95	0.96	0.98
CTE (0-300° C., × 10 ⁻⁷ /°C)	32.7	31.2	31.9	30.8	30.5	30.2	31.5	31.4
Dens. (g/cm ³)	2.416	2.404	2.394	2.38	2.37	2.355	2.375	2.367
Str. Pt (°C)	672	674	673	679	671	666	673	664
Ann. Pt. (°C)	727	731	729	734	728	729	729	720
Soft. Pt. (°C)	984	991	991	995	1001	1001	976	992
1110 BHf (mg/cm ²)	0.15	0.14	0.145	0.135	0.14	0.15	0.18	0.27
Liq. Temp. (°C)	1125	1120	1120	1125	1150	1135	1115	1140
Liq. Visc. (P)	5.04E+05	7.06E+05	6.34E+05	6.30E+05	3.66E+05	5.95E+05	5.30E+05	4.77E+05
Melt. Temp. (°C)	1659	1668	1650	1659	1668	1680	1635	1686

TABLE 1 (con't)

Composition Batched (mol%)	9	10	11	12 •	13	14	15	16	17
SiO ₂	69.1	69.65	68.75	69.1	68.8	69.33	69.65	70.05	69.33
Al ₂ O ₃	10.35	10.1	10.55	10.2	10.35	10.55	10.2	9.9	10.55
B ₂ O ₃	10.25	10.25	10.25	10.55	10.55	9.97	10.25	10.25	9.97
MgO	0.15	0.15	0.15	0.15	0.15	0.18	0.15	0.15	0.18
CaO	9.3	9.45	9.9	9.65	9.8	9.08	8.85	9.25	9.58
SrO	0.5					0.5	0.5		
BaO									
As ₂ O ₃	0.33	0.4	0.4	0.33	0.33	0.37	0.4	0.4	0.37
Sb ₂ O ₃									
CeO ₂									
Y ₂ O ₃									
SnO ₂	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
Cl									
RO/Al ₂ O ₃	0.96	0.95	0.95	0.96	0.96	0.93	0.93	0.95	0.93
CTE (0-300° C., $\times 10^{-7}/^{\circ}\text{C}$)	32.2	31.4	31.8	32	31.8	31.5	30.9	30.8	31.4
Dens. (g/cm ³)	2.377	2.366	2.371	2.364	2.366	2.376	2.369	2.357	2.366
Str. Pt (°C)	671	669	674	666	667	676	671	668	674
Ann. Pt. (°C)	727	725	729	722	723	731	728	726	730
Soft. Pt. (°C)	983	985	986	980	980	985	987	992	987
110 BHF (mg/cm ²)	0.15					0.12	0.12		
Liq. Temp. (°C)	1095	1090	1100	1090	1115	1095	1100	1100	1120
Liq. Visc. (P)	1.05E+06	1.23E+06	9.19E+05	1.07E+06	5.74E+05	1.19E+06	1.04E+06	1.12E+06	6.23E+05
Melt. Temp. (°C)	1649	1654	1650	1642	1650	1651	1657	1674	1654

TABLE 1 (cont')

	18	19	20	21	22	23	24	25	26
Composition Batched (mol%)									
SiO ₂	69.45	69.33	68.3	70.45	70	70.4	70.1	70	68.3
Al ₂ O ₃	11	10.55	10.9	9.85	10.35	10.05	10	10.23	10.9
B ₂ O ₃	9	9.97	10.4	9.55	9.5	9.69	10.15	9.75	10.4
MgO		0.18		1.1	0.8	0.82	0.81	0.8	
CaO	10	9.08	9.1	5.75	8.5	7.14	7.11	7	9.1
SrO		0.5	1	2.9	0.85	1.89	1.88	2.22	1.0
BaO									
As ₂ O ₃				0.4				0.3	
Sb ₂ O ₃	0.3	0.37	0.3						
CeO ₂					0.2	0.2	0.2	0.2	
Y ₂ O ₃									0.05
SnO ₂	0.05	0.02	0.05						
Cl	0.2		0.2						
RO/Al ₂ O ₃	0.91	0.93	0.93	0.99	0.98	0.98	0.98	0.98	0.93
CTE (0-300° C., $\times 10^{-7}/^{\circ}\text{C}$)	32	31.9	34.8	33.4	32.8	33.5	32.9	33.4	34.5
Dens. (g/cm ³)	2.386	2.383	2.403	2.405	2.378	2.378	2.374	2.391	2.392
Str. Pt (°C)	681	675	669	670	672	670	664	671	677
Ann. Pt. (°C)	737	730	725	727	728	727	720	727	732
Soft. Pt. (°C)	993	984	978	996	988	989	984	989	979
110 BHf (mg/cm ²)		0.16	0.3	0.39	0.18	0.17	0.19	0.19	0.19
Liq. Temp. (°C)	1150	1100	1140	1165	1160	1140	1150	1150	1150
Liq. Visc. (P)	2.90E+05	1.06E+06	2.40E+05	2.88E+05	2.49E+05	4.29E+05	2.80E+05	3.11 E+05	2.14E+05
Melt. Temp. (°C)	1642	1655	1617	1682	1656	1668	1653	1656	1620

TABLE 1 (con't)

Composition Batched (mol%)	27	28	29	30	31	32	Comp Ex
SiO ₂	68	70	70.4	69.8	71	72	67.6
Al ₂ O ₃	10.5	10	10.2	10.6	9.9	9.33	11.4
B ₂ O ₃	11	10	9.1	9	10	10	8.5
MgO							1.3
CaO	10.5	9	5.68	7.14	9.1	8.66	5.2
SrO			4.55	3.42			1.3
BaO							4.3
As ₂ O ₃							0.4
Sb ₂ O ₃	0.3	0.3	0.3	0.3	0.3	0.3	
CeO ₂							
Y ₂ O ₃							
SnO ₂							
Cl							
RO/Al ₂ O ₃	1.00	0.90	1.00	1.00	0.92	0.93	1.03
CTE (0-300° C., x 10 ⁻⁷ /°C)	34.9	32.0	34.4	34.4	32.1	31.2	37.8
Dens. (g/cm ³)	2.378	2.355	2.420	2.406	2.353	2.342	2.54
Str. Pt (°C)	659	673	669	672	669	672	666
Ann. Pt. (°C)	713	731	727	729	726	730	721
Soft. Pt. (°C)	967	999	987	984	998	1012	975
1110 BHF (mg/cm ²)	0.23	0.18					0.2
Liq. Temp. (°C)	1120	1130	1130	1135	1120	1125	1050
Liq. Visc. (P)	3.07E+05	5.99E+05	5.67E+05	4.38E+05	8.46E+05	8.79E+05	2.97E+06
Melt. Temp. (°C)	1611	1670	1671	1657	1685	1703	1636